

The Role of Impacting Processes in the Chemical Evolution of the Atmosphere of Primordial Earth

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ABSTRACT

The stability of the chemical composition of the planets' atmospheres on any time scale is determined by the ratio of source and sink strengths for various atmospheric constituents. Beginning with the Earth's formation and continuing throughout its history, these ratios have undergone significant alterations. Such changes are determined by various physical processes that are tied to the evolution of the Earth as a planet. A complete theory of the origin and evolution of the Earth's atmosphere is still far from complete at this time. This is due, in particular, to a certain randomness in the selection of a number of important physical parameters of the preplanetary cloud. They include, for example, the time scale for the dissipation of the gaseous nebula component; the planet accretion scale; and the chemical composition and distribution by size of planetesimals. It will therefore be useful to consider some physical constraints on the process by which the Earth's atmosphere was formed.

Currently existing paleontological data offer clear evidence of the presence of life on Earth 3.5 billion years ago (Schopf and Packer 1987). Furthermore, we can make the fundamental conclusion from the analysis of carbon isotope ratios $^{13}\text{C}/^{12}\text{C}$ that an almost contemporary biogeochemical carbon cycle (Schidlowski 1988) existed on Earth 3.8 billion years ago. Moreover, there is some reason to believe that this last dating could be pushed further back to four billion years (Schidlowski, personal communication). There is no doubt that both the prebiological evolution processes and the global biogeochemical carbon cycle can only occur in a sufficiently

dense atmosphere and hydrosphere that have already formed or are forming. Taking into account data from isotope systematics (Faure 1986), with which we can estimate the Earth's age at 4.55 to 4.57 billion years old, we conclude that the time scale for prebiological evolution and the emergence of life on Earth was sufficiently brief: possibly less than 0.5 billion years. This fact means, however, that the Earth's protoatmosphere must have been formed prior to the appearance of the biogeochemical cycle, that is, over a period of time significantly less than 0.5 billion years. Additional indirect evidence of the early emergence of the Earth's atmosphere can be found in analyzing the isotope relationships of the noble gases Ar and Xe (Ozima and Kudo 1972; Ozima 1975; Kuroda and Crouch 1962; Kuroda and Manuel 1962; Phinney *et al.* 1978).

Therefore, existing and observed data provide evidence of the very early formation of a dense atmosphere on Earth. We shall consider possible scenarios for the formation of the Earth's early atmosphere and its initial chemical composition.

EARTH'S INITIAL ATMOSPHERE

A model for Earth's early atmosphere, formed from solar composition gas captured gravitationally during the final stages of accretion, was explored in Hayashi's studies (1981, 1985). Hydrogen and helium are the primary components of this atmosphere. According to the estimates of several authors, the total mass of the initial atmosphere could have reached 10^{26} - 10^{31} g (Hayashi *et al.* 1985; Cameron and Pine 1973; Lewis and Prinn 1989). However, the inference by these models that the entrapment process occurred isothermally may lead to significant error: they overlook the heating up of the gas during accretion (Lewis and Prinn 1984). We will note that there are some additional difficulties in a model of an isothermal, initial atmosphere. They stem from the diffusive concentration of heavy gases in the initial atmosphere (Walker 1982). The pressure of the initial atmosphere for Earth is only 0.1 bar in the more realistic models of the adiabatic, gravitational capture of gas from a protoplanetary nebula (Lewis and Prinn 1984).

Clearly, an initial atmosphere could only have formed if the processes of gas dissipation from the protoplanetary nebula had not ceased by the time Earth's accumulation had concluded. Gas dissipation from a protoplanetary nebula is determined by a solar wind from a young T Tauri Sun and EUV (Sekiya *et al.* 1980; Zahnle and Walker 1982; Elmegreen 1978; Horedt 1978;). Canuto *et al.* (1983) have estimated the time scale for dissipation of the gaseous component of a protoplanetary nebula, using observed data on T Tauri star luminosity. Their estimates show that this time scale is not more than 10^7 years. It may only be several million years, beginning with

the onset of the convective phase in the history the Sun's development. This time scale is appreciably shorter than the approximately 10^8 years estimated for Earth's accumulation (Safronov 1969; Wetherill 1980). Hence, current theories of stellar evolution, coupled with observed astronomical data, raise the possibility that only a very weak initial atmosphere existed at the very inception of planets' accumulation process. This is a very serious argument against the formation of an initial atmosphere on Earth as proposed by Hayashi.

Nevertheless, one should note that the accuracy of estimates of the time scales for a significant portion of cosmogonic processes at the early stages of protosolar nebula evolution is not reliable enough to rule out, with absolute certainty, the possibility that an appreciable initial atmosphere existed on Earth. According to this scenario, the initial atmosphere encounters considerable additional difficulties stemming from its chemical composition. Adopting, again, the adiabatic model of the gravitational capture of gas from a protoplanetary nebula (Lewis and Prinn 1984), we can see that with a 0.1 bar value of the pressure of the primordial atmosphere, the nitrogen levels in it would be 10^5 times lower than present levels. At the same time, neon levels would exceed current neon atmospheric levels by approximately 40 times. Walker's more detailed computations, where he accounts for the radiative-convective structure of the primordial atmosphere (1982), also show an inconsequential pressure for this kind of atmosphere at the surface (approximately 0.2 bars). This means that arguments raised by Lewis and Prinn (1984) against a primordial atmosphere remain valid in this instance. Hence, various scenarios for a dense initial atmosphere appear to be highly improbable for the above reasons. Therefore, the very rapid formation of a dense Earth atmosphere was apparently a function of different physical processes.

CONTINUOUS DEGASSING

One of the suggested mechanisms for the rapid formation of the atmosphere is the intense, continuous degassing of Earth in the conventional sense of this term, including magmatic differentiation and volcanism (Walker 1977; Fanale 1971). There is still no answer to the question of whether continuous degassing of the Earth could have been intensive enough to allow for the formation of the atmosphere and the hydrosphere over a very short time span ($< 10^8$ years). Such a possibility exists where there is a strong, overall heating of the planet during its accretion. However, this entails the inclusion of a number of additional inferences regarding a very brief accretion scale: $< 5 \times 10^5$ years (Hanks and Anderson 1969).

Walker's recent analysis of the process of continuous degassing (Walker, this volume) shows that the present rate of degassing is clearly insufficient

to be responsible for forming the atmosphere in a very brief time scale. At the same time, Walker's proposed numerical estimate of the accumulation rate of hot lava on primordial Earth, which could have provided for the necessary intensity of degassing (1.3×10^{19} g/yr), appears to be unjustifiably high. Such intensive volcanism infers that $\sim 1.3 \times 10^{27}$ g of magma would pour out over 10^8 years of accumulation on the surface, or a quarter of the entire present mass of the Earth.

Under the currently adopted planetary accumulation models with an approximate 10^8 year time scale, such a hypothesis would only be justified in the case of a gigantic impact (Kipp and Melosh 1986; Wetherill 1986). There is no question that a considerable portion of the planet would have melted as a result of a gigantic impact which would have released a huge quantity of gases. This amount would have been sufficient to have formed an atmosphere. Yet, there is no detailed, physical-chemical model of this process at the present time. Furthermore, it cannot be considered that the very fact of a giant impact in the Earth's history has been firmly established. Clearly, if such a catastrophic event did actually take place in the earliest history of our planet, its consequences would have been so great that they would have been reflected in the geochemical "records." However, the scenario explored by Walker (this volume) of two reservoirs of volatiles, one of which is virtually entirely degassed (the upper mantle), and the other which has conserved its store of volatiles (lower mantle), is difficult to reconcile with the idea of a gigantic impact. Truly, such a clear separation of the two mantle reservoirs, whose presence has been determined with sufficient certainty from observed data (Allegre *et al.* 1987) is difficult to expect in the case of a gigantic impact. An attempt should be made to analyze the possible geochemical consequences of a gigantic impact and reconcile them with existing data. For now, a gigantic impact remains a reality only in computational models of the evolution of preplanetary swarms of bodies. However, this episode is only a specific case of the impact-induced degassing of matter. Yet impact-induced degassing was, apparently, a determining physical process which led to the very rapid formation of protoEarth's atmosphere.

IMPACT PROCESSES AND THE EARTH'S PROTOATMOSPHERE

The role of impact processes in forming Earth's protoatmosphere was discussed more than 20 years ago in Florensky's study (1965). During the years that followed, this idea was developed in a number of studies (Arrhenius *et al.* 1974; Benlow and Meadows 1977; Gerasimov and Mukhin 1979; Lang and Ahrens 1982; Gerasimov *et al.* 1985). Impact-induced degassing is rooted in the idea of Earth accumulation from large solids. This idea does not require the inclusion of any serious additional proposals. It is

this circumstance that brings us to the conclusion that impact degassing was a real mechanism in the formation of Earth's atmosphere and hydrosphere. Departing from the gigantic impact issue, we can see that the maximum dimension of those bodies which regularly fell on the planet, and from which Earth was formed, could have attained hundreds of kilometers (Safronov 1969). These dimensions fit with estimates of the diameters of impacting bodies which formed the largest craters on the terrestrial planets and their satellites (O'Keef and Ahrens 1977). The velocity of the collision of a random body of a preplanetary swarm with the embryo of primordial Earth is no less than the escape velocity. Therefore, the range of velocities of planetesimal collision with a growing planet embryo varies from meters per second at the initial stages of its expansion, to ≥ 12 kilometers per second at the final stages of accumulation. In reality, collision velocities could have been significantly higher in the case of a collision between Earth and bodies escaping from the asteroid belt, or with comets. In this case, when the mass of an expanding Earth reached approximately 10% of its current mass, the escape velocity became equal to roughly five kilometers per second; the melting of silicate matter began during a collision between planetesimals and an embryonic planet (Ahrens and O'Keef 1972). Beginning with the point where the mass of the embryo was equal to approximately 0.5 of the mass of present-day Earth, impact processes were paralleled by the partial vaporization of silicates (Ahrens and O'Keef 1972). The more high-speed planetesimals, reaching a speed of more than 16-20 kilometers per second, were completely vaporized. Several works (Ahrens and O'Keef 1972; Gault and Heitowit 1963; McQueen *et al.* 1973; Gerasimov 1979; O'Keef and Ahrens 1977) analyze in detail the physics of how colliding matter is heated as a shock wave passes through that matter and estimate the efficiency of impact-induced degassing. They demonstrate that impact degassing is most efficient when melting and partial vaporization of silicate matter begin. It is worth noting that the release of the primary volatile components begins long before the point when the planet's accumulation process reaches collision velocities corresponding to the melting point of matter. Pioneering works (Lang and Ahrens 1982, 1983; Katera *et al.* 1983) establish the beginning of volatile loss at extremely low collision velocities of approximately one kilometer per second. Using the Merchison meteorite as an example, the authors established that about 90% of the initial amount of volatiles is already lost at a collision velocity of 1.67 kilometers per second (Tuburczy *et al.* 1986). This loss is due to breakdown of the meteorite's water-, carbon-, and sulphur-containing minerals at impact. These experiments are proof of the beginning of volatile release at a very early stage of the Earth's accumulation. Its mass was less than 0.01 of its final mass. Water and carbon dioxide are the main constituents involved in the processes of shock-induced dehydration and decarbonatization of minerals.

As the mass of the embryonic planet increases, escape velocity rises. Consequently, there is also a rise in the velocity at which planetesimals fall. There occurs a corresponding increase in the heating of matter of the planetesimal and the surface of the planet in the central shock zone. The nature of degassing processes undergoes qualitative changes. The shock process becomes a considerably high-temperature one. Chemical reactions occurring in the vaporized cloud become increasingly significant. High-temperature chemical processes begin to play a predominant role during the final stages of Earth's accumulation, instead of the relatively simple processes involved in the breakdown of water-containing compounds and carbonates. Colliding matter undergoes total meltdown in the central zone of impact at collision velocities of five to eight kilometers per second: volatile components are released from the melted matter and interact with it. The chemical composition of the released gases must correspond to the volcanic gases for magma of corresponding composition and temperature. CO_2 , H_2O , and SO_2 will clearly be the primary components in such a gas mixture. The gases CO , H_2 , H_2S , CH_4 , and others may be competitors to these components, depending on the extent to which planetesimal matter is reduced (Holland 1964). Where collision velocities exceed eight to nine kilometers per second, vaporization at impact of a portion of planetesimal matter becomes significant.

Vaporization of silicate matter is supported by thermodissociation of planetesimal mineral constituents. As a result of this process, a considerable quantity of molecular and monatomic oxygen is released to the cloud of vaporized matter. Melt-vapor equilibrium determines the conditions for vaporization. The characteristic vaporization temperature for silicates is approximately 3000-5000 K. Vapor pressure is approximately 1-100 bars (Bobrovskiy *et al.* 1974). In these conditions, thermodynamic equilibrium in a gaseous phase is reached over a time scale $t_{chem} < 10^{-5}$ seconds (Gerasimov *et al.* 1985). Therefore, when large-scale impact episodes occur, where the characteristic time scale for the expansion of a cloud of vaporized matter t_{cool} is counted in seconds, thermodynamic equilibrium ($t_{cool} \gg t_{chem}$) is clearly reached at the initial stage of the expansion of such a cloud. Consequently, gases are formed in the cloud from the entire range of volatile elements present, regardless of what form they displayed in the initial matter. In such conditions, H_2O and CO_2 will be formed inside the dense, hot cloud if hydrogen, carbon, and oxygen are present in it. This will occur regardless of the initial presence in the planetesimals of carbonates and hydrated minerals. At the same time, where carbonates and hydrated minerals are present in planetesimals, a portion of the hydrogen and carbon in these minerals will be used to form other hydrogen- and carbon-containing components. Less H_2O and CO_2 will be produced than with the simple thermal breakdown of minerals. As

the vapor-gas cloud expands, its density and temperature drop, and t_{chem} increases. The expansion process commences when $t_{cool} \sim t_{chem}$. This is the point where the reaction products undergo chemical hardening, since the time scale for chemical reactions becomes greater than the characteristic time scale for cloud expansion as the cloud expands further. Gases with a chemical composition corresponding to the moment of hardening are mixed with atmospheric gases, interacting with both these gases and bedrock from the uppermost layers of the planet (regolith). If the atmosphere is dense, mixing of gases in an expanding cloud with atmospheric gases may occur earlier, when overall pressure of the expanding cloud $\rho v^2/2 + P$ (ρ = density, v = mass velocity, P = pressure in the vapor-gas cloud) becomes approximately the pressure in the atmosphere. The portion of the vaporized silicate matter α , which is condensed in the cloud by the time constituents harden (occurring at a given temperature T^*), is defined by the simple ratio (Anisimov *et al.* 1970):

$$\alpha \sim 1 - T^*/T_o,$$

where T_o denotes temperature in the vaporized cloud as it begins to expand. Estimates demonstrate that for impact of a planetesimal with a dimension of approximately 100 kilometers, the value is $T^* \sim 2000$ K. Therefore, for a vaporization temperature of $T_o \sim 5000$ K, the value is $\alpha \sim 60\%$. This means that approximately one half of molecular and monatomic oxygen, comprising $\sim 30\%$ of the cloud's pressure, (Gerasimov *et al.* 1985) will be released into the atmosphere with each impact. Clearly, the impact-vaporization mechanism is a powerful source of free oxygen in Earth's earliest atmosphere.

The chemistry of a high-temperature, gas-vapor cloud is too complex to be able to judge it solely in terms of the thermodynamical equilibrium in its gaseous phase. Condensation of silicate particles and catalytic activity occur during expansion and cooling of the vaporized cloud. These processes can significantly alter the equilibrating gas chemical composition. This circumstance imposes certain requirements on the search for both theoretical and experimental approaches to the study of chemical processes in a cloud of impact-vaporized matter.

Studies (Gerasimov *et al.* 1984; Gerasimov and Mukhin 1984; Gerasimov *et al.* 1987) used laser radiation to examine the chemical composition of gases which form during high-temperature, pulse-induced vaporization of the Earth's rockbed and meteorites. They demonstrated that molecular oxygen is actually the most abundant constituent in a cloud of vaporized matter (Gerasimov *et al.* 1987), and that it determines the chemical processes occurring in the cloud. Regardless of how reduced the initial matter is, the primary volatile elements H, C, and S are released as oxides: H_2O ,

CO, CO₂ (CO/CO₂ ≥ 1), and SO₂. In addition to the oxides, a certain amount of reduced components and organic molecules is formed in the cloud: H₂, H₂S, CS₂, COS, HCN, saturated, unsaturated, and aromatic hydrocarbons from CH₄ to C₆ and CH₂CHO. Molecular nitrogen is released. The vaporization-induced gaseous mixtures for samples belonging to both crust and mantle rock, as well as for conventional and carbonaceous chondrite, are qualitatively homogenous. This is seen in the preponderant formation of oxides, and in both the comparable (within one order of magnitude) ratios of the gases CO/CO₂ and the correlation between the various hydrocarbons. The gas mixtures formed at high temperatures are in nonequilibrium for normal conditions. Therefore, their chemical composition will be easily transformed under the impact of various energy sources.

One should note that the passage of a planetesimal through the atmosphere exerts a substantial influence on the formation of the atmosphere's chemical composition. Studies (Fegley *et al.* 1986; Prinn and Fegley 1987; Fegley and Prinn 1989) have analyzed this issue in the greatest detail in recent years. In the physics of the process, a body of large dimension (approximately 10 kilometers in diameter) passes through primordial Earth's atmosphere at a speed of approximately 20 kilometers per second; shock waves send a large amount of energy into the atmosphere. If we put the planetesimal density at ~ 3 g/cm³ (which matches the chondrite composition), and the angle of entry into the atmosphere at 45°, as first approximation, we would have 2.2×10^{27} ergs. This figure is 0.07% of the energy of an asteroid. The energy passes directly into the atmosphere as the body flies through, and even more energy (~ 3.2×10^{29} ergs) is "pumped" into the atmosphere by a supersonic discharge of matter from the impact crater (Fegley and Prinn 1989). The shock wave front (formed in the atmosphere during this process) compresses and heats the atmospheric gas to several thousand degrees Kelvin. It is clear that various thermochemical and plasmochemical reactions are occurring in this region. Due to recombination processes, new compounds are formed as cooling occurs. This substantially alters the initial chemical composition of the atmosphere.

We can estimate the chemical composition of the gas mixtures at high temperatures, using the standard methods of thermodynamical equilibrium (given the presupposition that the time scale for the breakdown of a given molecule is less than the time required to cool the elementary gas exchange). The most detailed computations of these processes were made in the studies of Fegley *et al.* (1986) and Fegley and Prinn (1989). It seems obvious that these findings must be critically dependent on the initial chemical composition of an unperturbed atmosphere. The atomic ratio C/O is an important parameter here: it determines the "oxidized" and "reduced" state of the atmosphere. Fegley and Prinn (1989) demonstrated that if

$C/O > 1$ (reduced atmosphere), precursors of biomolecules, such as HCN and H_2CO , are formed as the asteroid passes through this atmosphere. Nitrogen oxides appear in the oxidized atmosphere instead of prussic acid, supporting the formation of nitric acid if rain falls. Fegley and Prinn (1989) considered several possible chemical compositions for unperturbed atmospheres, and they calculated the commensurate alterations in the composition owing to the passage of large bodies through the atmosphere.

I would like to make the following comment regarding their work. The authors used computation methods employed for purely gaseous reactions. Heterogeneous catalysis on mineral particles (present in the atmosphere during the impact-induced discharge of matter) must play a significant role in the actual natural process. Heterophase reactions must considerably affect the evolution of the atmosphere's chemical composition during impact reprocessing. However, it is quite difficult to account for these reactions at this time. An account of the fluxes of such important components as prussic acid and formaldehyde is an unquestionable achievement in the work of Fegley and Prinn. Their efforts made it possible to estimate the stationary concentrations of these components in a modeled early atmosphere. We shall note that the numerical values of the strength of the source of cyanic hydrogen formation in atmospheric reprocessing and in experiments on laser modeling of the processes of shock-induced vaporization are comparable (Mukhin *et al.* 1989). Hydrocarbon and aldehyde output in the latter case is significantly higher.

THE EVOLUTION OF AN IMPACT-GENERATED ATMOSPHERE

Gas fluxes from the atmosphere present one of the most difficult issues related to the early evolution of the Earth's atmosphere. There are no accurate estimates at this time of the reverse fluxes of released gases to the surface rock of the young planet. It is therefore impossible to reliably estimate the stationary concentrations of these gases in the protoatmosphere.

The strength of a shock source of atmospheric gases is so great that the atmospheric accumulation of gases released during the fall of planetesimals at the early stage of accretion would create a massive atmosphere from water vapors. A runaway greenhouse effect would develop. Such a scenario was developed in several studies (Abe and Matsui 1985; Matsui and Abe 1986; Zahnle *et al.* 1988). The massive atmosphere "locks in" heat released by the impact. This in turn triggers the heating of the atmosphere and melting of the upper layers of the planet's silicate envelope. Zahnle *et al.* (1988) have estimated that the massive water atmosphere should condense and form an ocean as planetesimals cease falling. The problem however,

requires that all atmospheric components be taken into account, particularly CO_2 and SO_2 . These gases could also support a greenhouse effect, making it irreversible under the effects of solar radiation alone. The authors considered the processes of water dissolution in magma and thermal volatilization as examples of fluxes for water vapors. Lang and Ahrens (1982) looked at the hydration reactions of phorsterite and enstatite transported by planetesimals in order to determine H_2O flux rates. It should be noted that other flux mechanisms may be significant for primordial Earth.

An actualistic approach to the problem of fluxes is not entirely justified. To assess flux rates it is necessary to take into account physical-chemical conditions which correspond to the period of accumulation. One of the significant factors for the outflow of atmospheric gases to the regolith is the formation of a large quantity of condensed silicate particles from planetesimal matter vaporized during impact. With collision velocities of approximately 12 kilometers per second, approximately 30% of the matter in the central zone of impact is vaporized (Gerasimov 1979). Particle condensation takes place as the vaporized cloud expands and cools. These particles of small dimensions are discharged into the atmosphere, settle there, and fall to the surface of the accreting planet. Jakosky and Ahrens (1979) estimated rates of flux from the atmosphere for water vapor to a meter layer of regolith consisting of approximately 50 micron particles. Comparison of the rates at which water is released into the atmosphere during impact-induced degassing and absorbed by regolith has yielded a value approximately 0.008 bars for equilibrium pressure of water vapor in the atmosphere. This means that virtually all of the released water flows into the regolith. A similar view was put forward by Sleep and Langan (1981).

A structural-chemical analysis of condensed particles forming in model laser experiments (Gerasimov *et al.* 1988) has demonstrated that the condensed matter is nonequilibrium to a significantly great degree. It concurrently has phases with a high degree of silicon-oxygen tetrahedron (quartz type) polymerization and ostrov-type phases. It also includes silicon phases with an intermediary degree of Si^{2+} oxidation and metal silicon Si^0 . The condensed matter primarily contains oxidized iron FeO , as well as metal iron Fe^0 . These facts are possible evidence of high chemical activity of the condensed particles which form planets' regolith during accumulation. A number of experiments illustrate that the condensed particles in contact with water during heating may easily form laminated silicates that absorb appreciable quantities of water (Nuth *et al.* 1986; Nelson *et al.* 1987). Chemically active atmospheric gas components may also react with such regolith particles and have flux rates that are significantly higher than on present-day Earth with its oxidized crust.

The rapid (not more than a few seconds) and virtually complete

absorption by condensed particles of oxygen released during vaporization is an important experimental finding (Gerasimov 1987). This is evidence that, despite the impact-induced release of large amounts of oxygen into the atmosphere, molecular oxygen was absent in the primordial atmosphere: it was almost instantaneously absorbed by the regolith. It is possible that the same fate (albeit with greater time scales) is also characteristic for other chemically active gases. In the future, absorbed gases will be repeatedly released into the atmosphere owing to shock-induced processing of planet surface matter by falling planetesimals. Chemically inert gases, such as the noble gases and molecular nitrogen, may have accumulated in the protoatmosphere. Therefore, the degassing fate of noble gases and chemically active gases may have been entirely different (Gerasimov *et al.* 1985).

If we extrapolate the conditions on earliest Earth to the following period of "continuous" degassing, with a weaker source of atmospheric gases, atmospheric density would have been extremely small. This is due to the conservation of high flux rates. The appearance of a volatile-enriched (particularly oxygen) protocrust is one of the most important conditions for atmospheric stabilization. The appearance of an acidified protocrust ensures low flux rates for the majority of atmospheric gases and the accumulation of an ocean. In turn, the formation of an ocean also governs the composition and density of the atmosphere. The appearance of a protocrust is currently being considered in models of magmatic differentiation (Taylor and McLennan 1985). The earlier appearance of a protocrust in this model runs up against the same difficulties as the catastrophic formation of an atmosphere in the continuous degassing model. One possible avenue for the appearance of a protocrust is shock-induced differentiation (Mukhin *et al.* 1979; Gerasimov *et al.* 1985), as a result of which the atmosphere and the protocrust are formed within the same process of accumulation. However, the question of shock differentiation has yet to be theoretically analyzed in-depth and requires additional investigation.

The shock-degassing source was operative virtually throughout the planets' entire accumulation process. The formation of a sufficiently dense atmosphere at the earlier stages of accumulation of the Earth and the terrestrial planets is problematic owing to the possible rapid flux of atmospheric components to the regolith. Other factors also had an effect, such as shock-induced "cratering" of the atmosphere (Walker 1986), intensive T Tauri-like solar wind, EUV, and thermal volatilization. The probability of the formation of a dense atmosphere increases with the accumulation of the planet's mass, since by the time accretion is completed there is not likely to be any action of intensive solar wind and EUV. The loss of gases from a planet with a large gravitating mass is also difficult. Uncertainties in estimating the density of an impact-generated atmosphere at the final stage

of accretion are largely related to uncertainties in estimating the rates at which gases flow into the regolith.

Therefore, impact-induced degassing, despite the possible parallel input of an accretive source and a continuous degassing source was clearly the most probable and important source of atmospheric gases during the earliest epoch of the Earth's evolution: the period of its accumulation. Achievements made in recent years in investigating the impact source allow us to assess its strength and the chemical composition of the gases that were released. Nevertheless, the question of the evolution of the composition and density of the impact-generated atmosphere continues to remain an open one, primarily due to ambiguities in estimating gas flux rates from the atmosphere during accumulation. Therefore, it is our view that fluxes are one of the most important issues pertaining to the origin of Earth's earliest atmosphere.

REFERENCES

- Abe, Y., and T. Matsui. 1985. The formation of an impact-generated H_2O atmosphere and its implications for the early thermal history of the Earth. *Proc. 15th Lunar and Planet. Sci. Conf.*, part 2. *J. Geophys. Res. Supp.* 90:C545-C559.
- Ahrens, T.J., and J.D. O'Keef. 1972. Shock melting and vaporization of lunar rocks and minerals. *The Moon* 4:214-249.
- Allegre, C.J., T. Staudacher, and P. Sarda. 1987. Rare gas systematics: formation of the atmosphere, evolution and structure of the Earth's mantle. *Earth and Planet. Sci. Letters* 81:127-150.
- Anisimov, S.I., Ya.A. Imas, G.S. Romanov, and Yu.V. Khodyko. 1970. *The Effect of High-Power Radiation on Metals*. Nauka, Moscow.
- Arrhenius, G., B.R. De, and H. Alfvén. 1974. Origin of the ocean. In: Goldberg, E.D. (ed.). *The Sea*. Vol. 5. Wiley, New York.
- Benlow, A., and A.J. Meadows. 1977. The formation of the atmospheres of the terrestrial planets by impact. *Astrophys. Space Sci.* 46:293-300.
- Bobrovskiy, S.V., V.M. Gogolev, B.V. Zamyshlyayev, and V.P. Lozhkina. 1974. Break-away velocity in a solid medium under the effect of a strong shock wave. *The Physics of Combustion and Explosion* 6:891-89.
- Cameron, A.G.W., and M.R. Pine. 1973. Numerical models of the primitive solar nebula. *Icarus* 18:377-406.
- Canuto, V.M., J.S. Levine, T.R. Augustsson, C.L. Imhoff, and M.S. Giampapa. 1983. The young Sun and the atmosphere and photo-chemistry of the early Earth. *Nature* 305:281-286.
- Elmegreen, B.G. 1978. On the interaction between a strong stellar wind and a surrounding disk nebula. *Moon and Planets* 19:261-277.
- Fanale, F.P. 1971. A case for catastrophic early degassing of the Earth. *Chemical Geology* 8:79-105.
- Faure, G. 1986. *Principals of Isotopes Geology*. Sec. ed. Wiley, New York.
- Fegley, B., Jr., and R.G. Prinn. 1989. Chemical reprocessing of the Earth's present and primordial atmosphere by large impacts. In: Visconti, G. (ed.). *Interactions of the Solid Planet with the Atmosphere and Climate*, in press.
- Fegley, B., Jr., R.G. Prinn, H. Hartman, and G.H. Watkins. 1986. Chemical effects of large impacts on the Earth's primitive atmosphere. *Nature* 319(6051):305-308.
- Florenskiy, K.L. 1965. On the initial stage of the differentiation of Earth's Matter. *Geochemiya* 8:909-917.

- Gault, D.E., and E.D. Heitowit. 1963. The partition of energy for hypervelocity impact craters formed in rock. *Proc. 6th Hypervelocity Impact Symp.* 2:419-456.
- Gerasimov, M.V. 1987. On the release of oxygen from the intensively shocked meteorites and terrestrial rocks (abstract). Pages 320-321. In: *Lunar and Planetary Sci. 18*. Lunar and Planetary Institute, Houston.
- Gerasimov, M.V. 1979. On the mechanisms of impact degassing of planetesimals. *Letters to AJ.* 5(5):251-256.
- Gerasimov, M.V., Yu.P. Dikov, L.M. Mukhin, and V.I. Rekharsky. 1988. Structural-chemical peculiarities of the state of silicon in the processes of shock metamorphism (abstract). Pages 383-384. In: *Lunar and Planetary Sci. 19*. Lunar and Planetary Institute, Houston.
- Gerasimov, M.V., and L.M. Mukhin. 1984. Studies of the chemical composition of gaseous phase released from laser pulse evaporated rocks and meteorites materials (abstract). Pages 298-299. In: *Lunar and Planetary Sci. 15*. Lunar and Planetary Institute, Houston.
- Gerasimov, M.V., and L.M. Mukhin. 1979. On the mechanism forming the atmosphere of the Earth and the terrestrial planets at the stage of their accretion. *Letters to AJ.* 5(8):411-414.
- Gerasimov, M.V., L.M. Mukhin, Yu.P. Dikov and V.I. Rekharskiy. 1985. The mechanisms of Earth's early differentiation. *Vestnik of the USSR Academy of Sciences* 9:10-25.
- Gerasimov, M.V., L.M. Mukhin, and M.D. Nusinov. 1984. Study of the chemical composition of the gaseous phase formed under the effect of pulse laser radiation on certain rocks and minerals. *Papers of the USSR Academy of Sciences* 275(3):646-650.
- Gerasimov, M.V., B.L. Satovsky, and L.M. Mukhin. 1987. Mass- spectrometrical analyses of gases originated during impulsive evaporation of meteorites and terrestrial rocks (abstract). Pages 322-323. In: *Lunar and Planetary Sci. 18*. Lunar and Planetary Institute, Houston.
- Hanks, T.C., and D.L. Anderson. 1969. The early thermal history of the Earth. *Phys. Earth Planet. Interiors* 2:19-29.
- Hayashi, C. 1981. Formation of planets. Pages 113-128. In: Sugimoto, D., D.Q. Lamb, and D.N. Schramm (eds.). *Fundamental Problems in the Theory of Stellar Evolution*. IAU Symposium No. 93. D. Reidel, Dordrecht.
- Hayashi, C., K. Nakazawa, and Y. Nakagawa. 1985. Formation of the solar system. Pages 1100-1153. In: Black, D.C., and M.S. Matthews (eds.). *Protostars and Planets. II*. University of Arizona Press, Tucson.
- Holland, H.D. 1964. On the chemical evolution of the terrestrial and cytherian atmospheres. Pages 86-101. In: Brancazio, P.J., and A.G.W. Cameron (eds.). *The Origin and Evolution of Atmospheres and Oceans*-101. Wiley, New York.
- Horedt, G.P. 1978. Blow-off of the protoplanetary cloud by a T Tauri-like solar wind. *Astron. Astrophys.* 64:173-178.
- Jakosky, B.M., and T.J. Ahrens. 1979. The history of an atmosphere of impact origin. *Proc. Lunar. Planet. Sci. Conf.* 10:2727-2739.
- Kipp, M.E., and H. Melosh. 1986. Origin of Moon: A preliminary numerical study of colliding planets (abstract). Pages 420-421. In: *Lunar and Planetary Sci. XVII*. Lunar and Planetary Institute, Houston.
- Kotra, R.K., T.H. See, E.K. Gibson, F. Horz, M.H. Cintala, and R.H. Schmidt. 1983. Carbon dioxide loss in experimentally shocked calcite and limestone (abstract). Pages 401-402. In: *Lunar and Planetary Sci. 14th*. Lunar and Planetary Institute, Houston.
- Kuroda, P.K., and W.A. Crouch, Jr. 1962. On the chronology of the formation of the solar system. 2. Iodine in terrestrial rocks and the xenon 129/136 formation in the Earth. *J. Geophys. Res.* 67:4863-4866.
- Kuroda, P.K., and O.K. Manuel. 1962. On the chronology of the formation of the solar system. 1. Radiogenic xenon 129 in the Earth's atmosphere. *J. Geophys. Res.* 67:4859-4862.
- Lang, M.A., and T.J. Ahrens. 1983. Shock-induced CO₂ production from carbonates and a proto-CO₂-atmosphere of the Earth (abstract). Pages 419-420. In: *Lunar and Planetary Sci. 14th*. Lunar and Planetary Institute, Houston.

- Lang, M.A., and T.J. Ahrens. 1982. The evolution of an impact generated atmosphere. *Icarus* 51:96-120.
- Lang, M.A., and T.J. Ahrens. 1982. Shock-induced dehydration of serpentine: First quantitative results and implications for a primary planetary atmosphere (abstract). Pages 419-420. In: *Lunar and Planetary Sci. 13th.* Lunar and Planetary Institute, Houston.
- Lewis, J.S., and R.G. Prinn. 1984. Planets and their atmospheres: origin and evolution. In: Donn, W.L. (ed.). *International Geophysics Series*. Vol. 33. Academic Press, Inc., Orlando.
- Matsui, T., and Y. Abe. 1986. Evolution of an impact-induced atmosphere and magma ocean on the accreting Earth. *Nature* 319:303-305.
- McQueen, R., S. Marsh, J. Taylor, G. Fritz, and W. Carter. 1973. A formula for solid state based on the results of investigation into shock waves. Pages 299-427. In: Nikolaevskiy, B.N. (ed.). *High Velocity Impact phenomena*. Mir, Moscow.
- Mukhin, L.M., M.V. Gerasimov, and Yu.P. Dikov. 1979. Model of the Earth's accretive differentiation (abstract). Pages 876-877. In: *Lunar and Planetary Sci. 10.* Lunar and Planetary Institute, Houston.
- Mukhin, L.M., M.V. Gerasimov, and E.N. Safonova. 1989. Hypervelocity impacts of planetesimals as a source of organic molecules and of their precursors on the early Earth (abstract). In: *Lunar and Planetary Sci. 20.* Lunar and Planetary Institute, Houston.
- Nelson, R., J.A. Nuth, and B. Donn. 1987. A kinetic study of the hydrous alteration of amorphous MgSiO smokes: Implications for cometary particles and chondrite matrix. *Proc. 17th Lunar and Planet. Sci. Conf., part 2. J. Geophys. Res., Supp.* 92:E657-E662.
- Nuth, J.A., B. Donn, R. Deseife, A. Donn, and R. Nelson. 1986. Hydrous alteration of amorphous smokes: First results. *Proc. 16th Lunar and Planet. Sci. Conf., part 2. J. Geophys. Res., Supp.* 91:D533-D537.
- O'Keef, J.D., and T.J. Ahrens. 1977. Impact induced energy partitioning, melting, and vaporization on terrestrial planets. *Proc. Lunar Sci. Conf.* 8:3357-3374.
- O'Keef, J.D., and T.J. Ahrens. 1977. Shock effects during the collision of large meteorites with the Moon. The mechanics of funnel formation during impact and explosion. Pages 62-79. In: Ishlinskiy, A.Yu., and G.G. Cherniy (eds.). *Mechanika. What's New in Science from Abroad*, No. 12. Mir, Moscow.
- Ozima, M. 1975. Ar isotopes and earth-atmosphere evolution models. *Geochim. et cosmochim. Acta* 39:1127-1134.
- Ozima, M., and K. Kudo. 1972. Excess argon in submarine basalts and the Earth-atmosphere evolution model. *Nature Phys. Sci.* 239:23.
- Phinney, D., J. Tennyson, and V. Frick. 1978. Xenon in CO₂ well gas revisited. *J. Geophys. Res.* 83:2313-2319.
- Prinn, R.G., and B. Fegley, Jr. 1987. Bolide impacts, acid rain, and biospheric traumas at the Cretaceous-Tertiary boundary. *Earth Planet Sci. Letters* 83:1-15.
- Safronov, V.S. 1969. *Evolution of the Preplanetary Cloud and the Formation of the Earth and the Planets*. Nauka, Moscow.
- Schidlowski, M. 1988. A 3,800-million-year isotopic record of life from carbon in sedimentary rocks. *Nature* 333(6171): 313-318.
- Schidlowski, M. Private communication.
- Schopf, J.W., and B.M. Packer. 1987. Early arhean (3.3 billion to 3.5 billion-year-old) microfossils from Warrawoona Group, Australia. *Science* 237:70-73.
- Sekiya, M.K., Nakazawa, and C. Hayashi. 1980. Dissipation of the primordial terrestrial atmosphere due to irradiation of the solar EUV. *Prog. of Theor. Phys.* 64:1968-1985.
- Sleep, N.H., and R.T. Langan. 1981. Thermal evolution of the Earth: Some recent developments. *Adv. Geophys.* 23:1-23.
- Taylor, S.R., and S.M. McLennan. 1985. *The continental crust: Its composition and evolution*. Blackwell Scientific Publ, Oxford.
- Tyburczy, J.A., B. Frisch, and T.J. Ahrens. 1986. Shock-induced volatile loss from a carbonaceous chondrite: Implications for planetary accretion. *Earth and Planet. Sci. Letters* 80:201-207.
- Walker, J.C.G. 1990. Degassing. This volume.

- Walker, J.C.G. 1982. The earliest atmosphere of the Earth. *Precambrian Research* 17:147-171.
- Walker, J.C.G. 1986. Impact erosion of planetary atmospheres. *Icarus* 68:87-98.
- Walker, J.C.G. 1977. *Evolution of the atmosphere*. Macmillan, New York.
- Wetherill, G.W. 1986. Accumulation of the terrestrial planets and implications concerning lunar origin. Pages 519-550. In: Hartmann, W.K., R.J. Phillips, and G.J. Taylor (eds.). *Origin of the Moon*. Lunar and Planetary Institute, Houston.
- Wetherill, G.W. 1980. Formation of the terrestrial planets. *Ann. Rev. Astron. Astrophys.* 18:77-113.
- Zahnle, K.J., J.F. Kasting, and J.B. Pollack. 1988. Evolution of a steam atmosphere during Earth's accretion. *Icarus* 74:62-97.
- Zahnle, K.J., and J.C.G. Walker. 1982. Evolution of solar ultraviolet luminosity. *Rev. Geophys. Space Phys.* 20:280-292.